PREPARATION OF ALUMINIUM NITRIDE

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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PREPARATION OF ALUMINIUM NITRIDE

A THESIS

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THE PREPARATION OF ALUMINIUM NITRIDE.

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Theoretically when aluminium oxide is heated to a high temperature with carbon in the presence of nitrogen, the following reaction takes place:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

However this reaction is by no means complete and considerable amounts of undecomposed materials remain in the charge.

It will be seen that from the above equation the proportions for the amounts of aluminium oxide and carbon are in the ratio of one part of aluminium oxide to .353 parts by weight of carbon. This theoretical ratio seems to be the best in practical work. If the reaction were complete the preduct would be a white amorphous material with little undecomposed carbon and samples giving a high percentage of nitrogen answer to this description.

Theoretically, the best temperature for the reaction would be just below 2200° C., which is supposed to be the decomposition temperature of the nitride. This is not true, however, as other experimenters have shown that the correct temperature is much lower.

The following extract on the preparation of aluminium nitride as carried out by Serpek is taken from "The Fixation of Atmospheric Nitrogen" by Joseph Knox; and gives the essentials of the most successful part of Serpek's work:

"Serpek's Aluminium Nitride Process.- The only process depending on the formation of a metallic nitride which at present seems to offer prospects of technical success is that devised by Serpek, which depends on the production of aluminium nitride from alumina, and subsequent decomposition of the nitride. Serpek at first used powdered aluminium carbide as raw material, and heated this in a current of nitrogen or generator gas. The absorption of nitrogen was said to be increased by the addition of carbon or aluminium to the carbide, and by the presence of traces of SO_2 or HCl in the gas current. Caro showed that the absorption of nitrogen by Al_4C_3 was probably preceded by dissociation of the carbide into aluminium and carbon.

Later a mixture of alumina and carbon (coal) was

heated in a current of nitrogen or generator-gas to red heat. The formation of the nitride takes place according to the theoretical equation. The addition of five per cent copper or iron facilitated the absorption, and the action of these metals was regarded as catalytic. In this case also the presence of traces of SO_2 or HCl was said to favor absorption of nitrogen. Serpek assumed that Al_4C_3 was first formed, which then reduced the remaining Al_2O_3 to aluminium, which combined with the nitrogen:

$$Al_4C_3 + Al_2O_3 = 6Al + 3CO,$$

$$6Al + 3N_2 = 6AlN.$$

Further investigation showed that the yield of nitride depended greatly on the temperature employed. It was found that some absorption of nitrogen took place even at 1100°C.; at 1500° nitrogen was absorbed fairly rapidly; at 1700° energetically; and at 1800-1850° almost violently, giving nearly chemically pure nitride. Smaller yields were obtained at higher temperatures, and above 2000° C. the production of nitride practically ceased, owing to decomposition of the nitride. The

most favorable temperature is, therefore, 1800° - 1900° C. It was also found that impure alumina, such as bauxite, could be converted into nitride at somewhat lower temperatures than pure, evidently owing to the catalytic effect of the impurities."

The commercial process as carried out in France is omitted as it is merely a technical description, and contains no statements of scientific interest.

"Scientific Investigation of the Serpek Process.- Remarkably few scientific investigations of the reaction involved in the Serpek process have appeared. Tucker and Read found that the absorption of nitrogen by a mixture of alumina and carbon was very slight below 1600° C., reached a maximum between 1800 and 2000° C., whilst decomposition of the AlN seemed to occur. The formation of the nitride takes place according to the equation:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

Serpek's statement that bauxite reacts more readily than pure alumina was confirmed, but it was found that the presence of appreciable amounts of SO_2 in the nitrogen was harmful.

An important contribution to the subject was recently made by Fraenkel, who gives also a very complete bibliography of the earlier literature on aluminium nitride. Fraenkel studied the velocity of absorption of pure dry nitrogen by a mixture of 2 parts pure alumina and 1 part finely divided pure soot, and found that the velocity of absorption is very small at 1350°, increased moderately up to 1500°, and very rapidly above 1500°. Thus in thirty minutes .2 per cent N_2 was absorbed at 1350°; 3.1 per cent at 1400°; 4.4 per cent at 1450°; 8 per cent at 1500°; 19.5 per cent at 1550°; and 24.5 per cent at 1600°. Up to 1500°, the amount of nitrogen absorbed is approximately proportional to the time, but at higher temperatures the reaction goes quickly at first, and then, after a large proportion of the charge has reacted, slows down considerably.

According to Peacock and Du Pont a mixture of 3 parts of alumina and 1 part of carbon reacts with nitrogen under 500 mm. pressure at 1500° according to the equation:

$$Al_2O_3 + 6C + 3N_2 = Al_2C_3N_6 + 3CO.$$

Fraenkel obtained no indication of such a reaction, but

found that at pressures down to 250 mm. the velocity of the reaction was practically the same as at atmospheric pressure.

A different result is obtained if the partial pressure of the nitrogen is lowered by mixture with another gas, especially CO, the product of the reaction. If we regard the reaction:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO,$$

as revereible, the law of mass-action gives $C_{N_2}/C^3_{CO} = K$. The reversibility of the reaction was proved by passing different mixtures of N_2 and CO at a given temperature either over a mixture of alumina and carbon, or over a mixture containing a certain proportion of AlN, and determining the percentage of nitrogen in the mixture before and after passing the gas. When the proportion of CO in the gas mixture was above a certain amount, the percentage of nitrogen in the solid diminished, showing that the reaction from right to left was taking place. When the proportion of CO was below a certain amount, nitride formation took place. The results show distinctly that an equilibrium exists, but it was not possible to define it accurately. At a total pressure of

1 atmos. the equilibrium concentration of CO at 1500° is between 25 per cent and 40 per cent CO, and at 1600° between 50 per cent and 65 per cent CO. At 1700° active absorption of nitrogen still took place from a gas containing 70 per cent CO. With increasing temperature the equilibrium concentration of CO, therefore, increases. This result is important technically. If generator gas is used, a higher temperature is required than with pure nitrogen, and the higher the temperature the less pure does the nitrogen require to be. Further, with generator gas it is useless to look for catalysts for the reaction in the neighborhood of 1500°. These can be effective only with nitrogen containing less CO than generator gas.

A shifting of the equilibrium with temperature in the direction found indicates that the reaction from left to right is endothermic. In afreement with this, Fraenkel calculated the heat of this reaction to be ca. - 243000 cals., and Richards - 213220 cals. The reaction is, therefore, strongly endothermic.

As a result of a preliminary investigation of the influence of different forms of carbon and of various

catalysts on the velocity of the reaction Fraenkel states, with all reserve, that different forms of carbon show essential differences in reaction-velocity, and that none of the catalysts so frequently mentioned in the Serpek patents show any marked influence on the reaction-velocity in the neighbourhood of 1500°.

The Badische Anilin-und Soda-Fabrik has also investigated the technical production of aluminium nitride. They find that the formation of nitride from alumina and coal is greatly accelerated by the presence of 5-10 per cent of the oxides of certain elements which themselves can form stable nitrides. Under these conditions it is possible to secure rapidly and easily a fairly high percentage of nitrogen in the product. Among the oxides which may be used are those of Si, Ti, Zr, Mo, V, Be, Ce, Ur, Cr. Preference is given to SiO_2 on account of its cheapness, but under certain local conditions some of the others might be used with advantage, especially as they are recovered and can be used again. The oxides may be replaced by other oxygen compounds, such as silicates, titanates, vanadates, etc. The presence of iron and other impurities does not influ-

ence the catalytic action, so that low-grade bauxite may be employed.

The Badische has also worked out methods of treating the crude nitride, so that, whilst the ammonia is completely recovered, the aluminium is obtained in the form of a pure compound. Thus by treating the crude aluminium nitride, containing, for example, silicon nitride, with limited amounts of acid or alkali, the aluminium may be obtained as a soluble compound, free from silica. The quantity of acid or base can also be chosen so that the aluminium remains as insoluble hydroxide:

$$2AlN + H_2SO_4 + 6H_2O = 2Al(OH)_3 + (NH_4)_2SO_4.$$

The elimination of ammonia by alkalies is greatly facilitated by the addition of such soluble salts as sodium chloride."

Thru the courtesy of Prof. Harry McCormack of the Chemical Department, Armour Institute of Technology, the following results are quoted. In his experiments, Prof. McCormack used the same furnace which was used in the experimental part of this work. He found that, if all conditions were kept constant except the temperature, the best yield of nitrogen was obtained at from 1775° to

1825° C. Therefore, this temperature was taken so as to secure the best results in the particular furnace used.

Prof. McCormack also made several runs at the above temperature, taking out samples at various increments of time in order to determine the length of time the charge should be in the furnace to secure the best absorption of nitrogen. In this work, the furnace was first brought up to the required temperature with the container enclosed so that the latter would be at furnace temperature. A cold sample was then put into the container and at the end of twenty minutes the first sample withdrawn. Samples were withdrawn for every subsequent interval of fifteen minutes with the following results:

Time in minutes	%N, run #1	%N, run #2.
20	4.1	5.6
35	12.2	11.9
50	10.9	12.4
65	10.5	11.7
80	12.14	9.4
95	10.6	----

The conclusion reached in this case was, that the correct amount of time for the charge to be in the furnace at the required temperature is from 30 to 35 minutes; and that if it was left in the furnace for a longer period a partial decomposition would take place decreasing the amount of nitrogen absorbed.

He also found out that with pure Al_2O_3 and coke at a temperature of 1900° C. for forty minutes, that the yield of nitrogen was 3.57%; and that another charge containing an aluminous ore containing some iron introduced, immediately after the first was withdrawn, and subjected to the same conditions absorbed 12 per cent nitrogen. Thus it was concluded from this work that a small amount of impurities increased considerably the amount of nitrogen absorbed, all other conditions being the same.

The following patents, recently taken out for the manufacture of aluminium nitride, are quoted from "Chemical Abstracts" for 1917 and 1918:

"Aluminium nitride; electric furnaces. Soc. Generale des Nitrures. Brit., 11,271. Aug. 4, 1915. Nitrogen,

like producer gas, and the like, used in the production of AlN is heated to a temperature adjacent to or above that of the reaction, and then mixed with the aluminous material and carbon, the mixture being acted on for a very short time by an arc or other source of intense heat. The heating of the gas may be effected, in a suitable furnace (specified) by a high pressure arc between electrodes in a small chamber, from which the arc is blown into the gas passage. Gaseous products may be burnt for preliminary heating of the nitrogen, etc. The aluminous material and carbon, which are fed by a tube in the shaft, may also be preheated as by conduction from adjacent gas heaters. From the shaft, the material passes to a chamber, into which the gas is conveyed by pipes bent horizontally so as to produce whirling motion.

Aluminium nitride. Soc. Gen. des Nitrures. Holl. 1279. January 15, 1917. In this process the aluminium oxide plus excess carbon form the heating resistance in an electric furnace.

Norske Nitride Aktiesel skab. Norw. 27,628. Jan. 8, 1917. Reaction mixture consisting of bauxite mixed

with coal is acted upon by a flame produced by the combustion of an excess of coal in air to produce CO, the flame being heated by passing thru one or more electric arcs.

G. Giulini. Norw. 27,618. Feb. 5, 1917. The nitrogenous gases are brought to act on the initial substances in the presence of sodium vapor, at an elevated temperature but not so high as to require electrical energy.

O. Serpek. U. S. 1233925. July 17, 1917. In forming AlN from carbon and bauxite or other aluminous material by reaction with nitrogen, the latter is highly heated before being brought into contact with other materials, and the mixture is then rapidly passed thru an elongated electric arc.

AlN. O. Serpek. U. S. 1233926. July 17,1917. A flame is produced by the combustion of such excess of carbon in air that CO is the main product and this flame is caused to enter the reaction zone of an electric arc together with an excess of carbon and Al_2O_3 or other aluminiferous material to form AlN.

AlN. P. Bunet. Can. 173693. December 5, 1915.

The reaction materials are caused to advance thru an inclined revolving electric furnace which two conductive crowns, and intermediate electrodes.

AlN. P. R. Hershman. U. S. 1250874. Dec. 18. Aluminium nitride is formed by heating a charge of Al_2O_3 and C in the reaction chamber by passing producer gas pr eviously heated to a high temperature thru the charge, burning a portion of the gas in the charge and then effecting nitrification by continuing the passage of producer gas thru the material.

AlN. H. L. Duncan. Can. 182,348. Feb. 19,1918. Aluminous material is heated in a nitrogenous reducing atmosphere in a rotary kiln by means of a luminous heating flame and a high pressure jet of nitrogenous gas is caused to impinge on the heated material to produce aluminium nitride.

AlN. M. Shoeld. U. S. 124797. August 6. AlN is made by bringing briquets composed of carbon, alumina and a binder into contact with a counter current of nitrogen carrying gas. An intermediate zone of the charge only, in heated to 1800-2000°C. electrically which also effects preliminary heating of reacting

materials by the counter-current principle. (Furnaces were designed by the above on this principle for this purpose)."

Serpek has taken out the greatest number of patents both in this country and abroad on this subject and they are too numerous to mention here. The most promising part of his work, both experimentally and commercially, has been described in the extract from "Fixation of Atmospheric Nitrogen" by Joseph Knox.

There are also numerous other patents which have been taken out prior to the ones mentioned here, but it is presumed that they offer no extension of the knowledge of the formation of aluminium nitride. On that account only the recent, untried ideas have been mentioned.

The electric furnace used in this work was a Hoskin's carbon resistance type. It consists of a reaction tube about three inches internal diameter, and about two feet long. This is made of carborundum about one fourth inch thick. Surrounding this tube are the carbon rings forming the heating and resistance element. These are about an inch wide and onefourth inch thick. These rings are placed side by side and clamped by a stationary electrode on one end, and by a movable one on the other. The purpose of the latter is to regulate the pressure between the carbon rings and hence the amount of current flowing thru the furnace. Outside of the carbon rings is another tube of refractory material. Between this tube and the iron case is a space which is filled with silicon dioxide.

Alternating current is supplied thru a transformer to the furnace at a potential of approximately 220 volts. One hundred sixty amperes is the maximum demand which may be taken from the transformer. All regulations of current are taken care of by adjusting the pressure between the carbon rings in the furnace.

The charge as a whole was made up of wood charcoal,

chemically pure aluminium oxide and chemically pure ferric oxide. The wood charcoal was the ordinary commercial charcoal. This was ground to a fine powder in an iron mortar, so that the charge could be very intinately mixed. The aluminium oxide and ferric oxide were weighed out so that the total of the weights equaled ten grams. To each charge so prepared an equal quantity of charcoal: 3 grams was added so that the total weight of the charge was thirteen grams. The percentage of ferric oxide in each charge was figured on the total weight of ferric oxide and aluminium oxide only.

Eighteen separate charges were thus weighed out and each was thoroughly mixed and ground together in a cassarole before introduction into the furnace. The weighings in each case were made on the laboratory balance accurate to a tenth of a milligram so that the amount of iron may be calculated on any basis very accurately.

The following table shown on the next page gives the weights of the separate constituents and also the percentage of iron oxide on the basis stated above:

Charge	Gr. Al_2O_3	Gr. Fe_2O_3	Gr. C.	$\%Fe_2O_3$
# 1	9.9500	.0500	3.0000	.5
# 2	9.9000	.1000	3.0000	1.0
# 3	9.8500	.1500	3.0000	1.5
# 4	9.8000	.2000	3.0000	2.0
# 5	9.7500	.2500	3.0000	2.5
# 6	9.7000	.3000	3.0000	3.0
# 7	9.6500	.3500	3.0000	3.5
# 8	9.6000	.4000	3.0000	4.0
# 9	9.5500	.4500	3.0000	4.5
#10	9.5000	.5000	3.0000	5.0
#11	9.4500	.5500	3.0000	5.5
#12	9.4000	.6000	3.0000	6.0
#13	9.3500	.6500	3.0000	6.5
#14	9.3000	.7000	3.0000	7.0
#15	9.2500	.7500	3.0000	7.5
#16	9.2000	.8000	3.0000	8.0
#17	9.1500	.8500	3.0000	8.5
#18	9.1000	.9000	3.0000	9.0

Charges referred to by numbers mean the numbers as assigned in the first column.

The boat on which the charges were placed prior to their introduction into the furnace was made of carbon. In order to facilitate the handling of as great a number of charges in the shortest time, two partitions were placed in the boat so that the charges could be introduced into the furnace in groups of three. These partitions consisted of carbon sticks about one fourth inch high and one half inch wide and served only to keep the charges from mixing together in the furnace.

The first three charges were placed in the boat, that is, charges #1, #2, and #3, and were placed in the furnace which was at room temperature. The gas was then turned on so that a very gentle stream was produced. The gas used was obtained from a tank of compressed nitrogen. The electrodes were screwed down tight and the current turned on. The temperature at the end of thirty minutes was 1600-1700^{0} C. and the current consumption one hundred sixty amperes. The charge was with drawn thirty-five minutes after the furnace had reached the temperature above mentioned, and allowed to cool in the air. Then it was placed in weighing bottles for analysis.

The second group of charges, #4, #5, and #6 was placed in the furnace at 11:45 A.M. at a bright red heat and ten minutes were allowed for the furnace to reach the correct temperature. The gas stream was never adjusted after the first charge was placed in the furnace so that it would be constant thruout. This group was removed at the operating temperature and immediately placed in weighing bottles before attaining room temperature. Time of removal: 12:30 P.M.

The third group, #7, #8, and #9, was introduced into the furnace at operating temperature at 12:45 P.M. and with drawn at 1:30 P.M. These were allowed to cool pretty thoroughly in the air before putting them in the weighing bottles.

#10, #11, and #12 were also introduced at the operating temperature and withdrawn thirty-five minutes later. These were also allowed to cool to a black heat before putting them in the weighing bottles. The fifth group was also placed in the furnace under the same conditions except that it was in the furnace for only thirty minutes. It was, however, transferred to the weighing bottles hot.

The sixth and last group, consisting of charges #16, #17 and #18 was introduced into the furnace at the operating temperature at 3:40 P.M. At 4:10 P.M. the current was shut off and the charges were allowed to cool in the furnace and finally transferred to the weighing bottles warm.

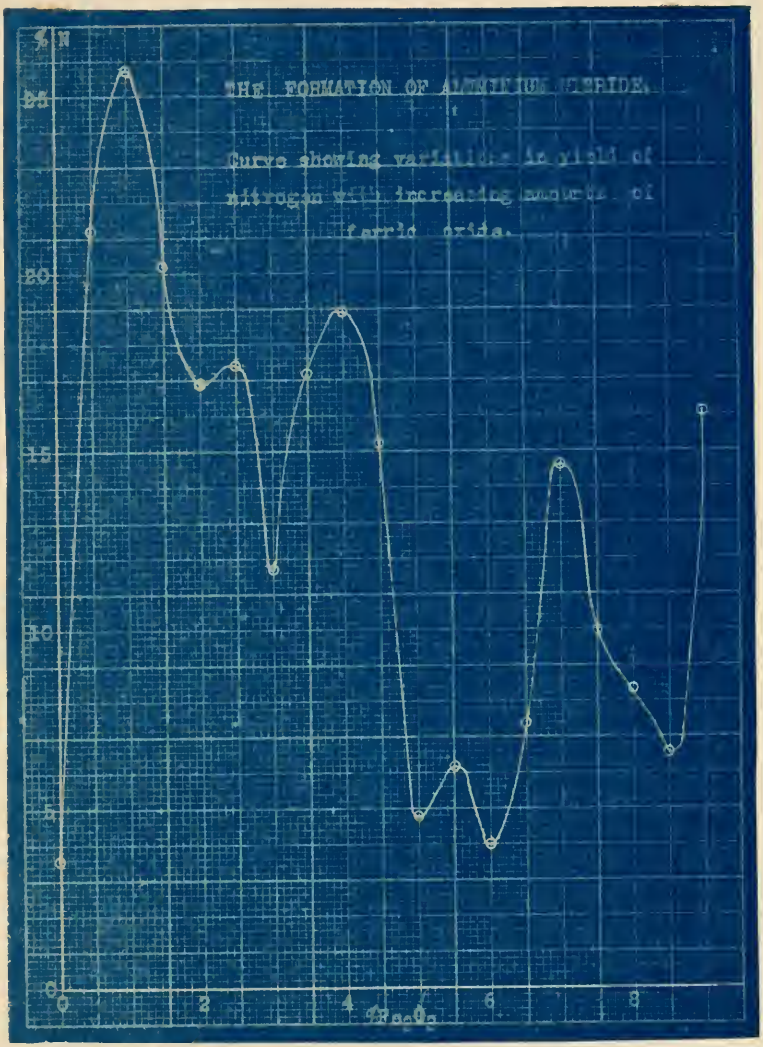
The charges were always placed in numerical order in the boat and their position in the furnace was such that the largest of the three numbers was always nearest the end of the furnace where the nitrogen entered. In each case it was noticed that some of the charges nearest the gas end were blown across the last two by the gas stream, but this occurred to such a slight extent that such contamination would have little effect on the amount of nitrogen absorbed. The separate charges were very carefully separated in each case to avoid contamination as much as possible.

The rate of flow of the nitrogen was practically constant thruout all of the heats. The end of the furnace into which the nitrogen was introduced, was so constructed so that no air could enter with it and a pure nitrogen atmosphere was maintained.

The charge immediately after removal from the furnace whowed that a crust of hard, dark gray material was formed on the surface in each case. In some instances the color was almost white, whereas in others, dark gray. In the darker samples small particles of undecomposed carbon could be distinguished showing that the carbon was in excess, or the reaction was not complete. In every case, the lighter colored compound gave a higher percentage of nitrogen than the darker, demonstrating that an excess of the aluminous material gave better results than an excess of carbon.

The samples thus obtained after heating were analyzed by the Kjeldahl process which gives the total in each charge. No attempt was made in order to find out how much nitrogen could be hydrolyzed from the samples. The table on the following page shows the results of the analysis. A curve was also plotted from these results to show the variation in the absorption with the variation of the amount of ferric oxide in the charge.

Charge	$\%Fe_2O_3$	% total N.
#1	.5	21.20
#2	1.0	25.70
#3	1.5	20.20
#4	2.0	16.90
#5	2.5	17.40
#6	3.0	11.67
#7	3.5	17.15
#8	4.0	18.90
#9	4.5	15.20
#10	5.0	4.75
#11	5.5	6.17
#12	6.0	4.00
#13	6.5	7.37
#14	7.0	14.60
#15	7.5	9.95
#16	8.0	8.37
#17	8.5	6.57
#18	9.0	16.07



THE FORMATION OF ALUMINIUM NITRIDE.

Curve showing variation in yield of nitrogen with increasing amounts of ferric oxide.

It is seen that from these results, iron oxide plays a very important part as a catalyst in the reaction. Contrary to all previous results, this work shows that only a small percentage of iron is necessary in order to bring about a maximum yield. It must be borne in mind, however, that chemically pure alumina and ferric oxide were used thruout the experimental work, and that, with commercial aluminous ore containing perhaps smaller quantities of other impurities besides iron, better results could be obtained. It must also be remembered that a practically pure nitrogenous atmosphere was maintained in the reaction tube and the only other gas present was carbon monoxide, a product of the reaction.

From the fact the maximum yield occurred when the proportion of alumina and carbon were nearly theoretical, the conclusion may be drawn that only a little excess of carbon is necessary for the best results. The ratio of Al_2O_3 to 3C is 102.2 to 36.0 or 2.84. The ratio of the weights of alumina and carbon, in the charge showing the maximum yield of nitrogen, is 9.9 to 3 or 3.3. The ratio of the weights on every other case with the exception of the first sample is greater.

It is the belief of the writer that these results thus obtained could be duplicated under the same conditions, and that possibly, on a commercial scale, bettered. The last statement is added because it has been shown by other experimenters that a better yield of nitrogen is obtained with commercial alumina than with chemically pure aluminium oxide.

Prof. McCormack of Armour Institute of Technology has worked out the best conditions for the operation of the particular furnace used here, and he has given the results of the work in order to secure the best operation of the process.